Europäisches Patentamt

Eur pean Patent Office

Office europé n des br vets



(11) EP 0 566 790 B1

(12)

# **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:07.08.1996 Bulletin 1996/32

(51) Int Cl.6: H01F 1/11

(21) Application number: 92303640.4

(22) Date of filing: 23.04.1992

(54) Magnetic powder and magnetic toner Magnetpulver und magnetischer Toner Poudre magnétique et toner magnétique

(84) Designated Contracting States: **DE FR GB NL** 

(43) Date of publication of application: 27.10.1993 Bulletin 1993/43

(73) Proprietor: TODA KOGYO CORP. Hiroshima-shi Hiroshima-ken (JP)

(72) Inventors:

Okano, Yoji Hiroshima-shi, Hiroshima-ken (JA)

 Fujioka, Kazuo Hiroshima-ku, Hiroshima-ken (JA)

 Aoki, Koso Hiroshima-shi, Hiroshima-ken (JA) Misawa, Hiromitsu
 Hiroshima-shi, Hiroshima-ken (JA)

 Kurita, Eiichi Hiroshima-shi, Hiroshima-ken (JA)

Fujii, Yasuhiko
 Otake-shi, Hiroshima-ken (JA)

(74) Representative: Woods, Geoffrey Corlett
 J.A. KEMP & CO.
 14 South Square
 Gray's Inn
 London WC1R 5LX (GB)

(56) References cited:

FR-A- 2 353 619

US-A- 3 535 245

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

This invention relates to a magnetic particle powder included in magnetic toners used for magnetic image character

# D scription

information can be read on the surface of a personal check or other document bearing images formed by ordinary which can preferentially be used in MICR are also being carried out intensively. MICR is a technique wherein encoded referred to as MICR, is coming to be paid attention attractively, and developments and research of the magnetic toners developers such as magnetic toners and carriers. In recent years, magnetic image character recognition, hereinafter powder and an organic polymer was already employed in magnetic printing materials and electrostatic latent image or novel functions have actively been pursued. Among them, a composite material comprising a magnetic particle Researches on the complexing of different materials to provide a new composite material with high performance recognition, which enables the formation of fine accurate images and the exact detection of encoded informations.

magnetic toners that would enable the ordinary character images and the readable encoded images to be formed terms of workability and economic viability. To resolve these problems, a great need has arisen in recent years for as the ordinary characters and encoded characters could not be printed at the same time, serious problems arose in planography, different inks had to be used for the ordinary character images and for the encoded images. Furthermore, It is particularly widely used for inspecting personal checks in bank clearing houses. In conventional typography and characters and images formed and encoded by special numerals or characters to collect and identify such informations.

numerals or images encoded by special characters in fine detail. Furthermore, it must also be possible to read the ordinary characters in the same way as toners used in the electrostatic image developers, but also of forming special The magnetic toners used in MICR, as described hereinbefore, must therefore be capable not only of forming simultaneously by laser beam printers which are now rapidly coming into wide use.

It is particularly important to provide a better reliability when reading the encoded images. This requires a fine encoded images accurately.

so as to obtain toners with the desired properties. improvements in the magnetic particle powders having a direct effect on the magnetic toners used to form the images requires that signal levels conform as far as possible to nominal signal levels. There was therefore a great need for image quality with little background and as high an image density as possible. Also, the accurate reading of images

as acicular magnetite or "Mapico Black" supplied by Cities Services Co., as described in US-A-4517268. Conventionally, the magnetic particle powders used in MICR magnetic toners were particulate magnetites such

these requirements however had not yet been produced using the conventional magnetic particle powders such as enable the formation of fine accurate images and the exact detection of the encoded informations. A toner fully satisfying At present, there is a great need for new magnetic particle powders for the magnetic toners of MICR, which would

magnetic toners used for MICR so as to enable the formation of fine accurate images and the exact detection of the The object addressed by this invention is thus to obtain a magnetic particle powder which is to be included in the the conventional acicular magnetite or "Mapico Black".

20 emu/g) contains from 18.5 to 22.5 % by weight of Fe<sup>2+</sup> based on the total weight of the powder and has a specific with silicon oxide, aluminium oxide or a mixture thereof, has a residual magnetization of from 12 to 20 Am<sup>2</sup>/kg (12 to The present invention therefore provides a magnetic particle powder which comprises magnetite particles coated

In the accompanying drawings: surface area of from 3.5 to 9.5 m<sup>2</sup>/g.

as an intermediate for producing the preceding magnetite particles. product obtained by the present invention with saturation magnetization of maghemite/hematite composite particles Fig. 1 hereinafter referred to indicates the relation of residual magnetization of the magnetite particles as a final

likewise be identified. In view of the reading reliability, the magnetic particle powder should preferably have a residual cannot be identified. If it is greater than 20 emu/g, the output is above a suitable level so that the characters cannot it is less than 12 emu/g, a suitable output is not obtained when the encoded images are to be read so that the characters The residual magnetization of the magnetic particle powder according to the invention is from 12 to 20 emu/g. If The invention is hereinafter described further in detail with referring to preferred embodiments.

by weight. From the viewpoint of clarity of the image density, the amount of Fe2+ should preferably be from 19.5 to higher density than that given by the conventional magnetic toners, it is sufficient if the upper limit of Fe<sup>2+</sup> is 22.5 % than 18.5 % by weight, the output image has a reddish tinge which is undesirable. To obtain a deep black image of The amount of Fe<sup>2+</sup> in the magnetic particle powder of this invention is from 18.5 to 22.5 % by weight. If it is less .e\uma 6.8t of St mont to noitssitengem

resin, the image density is reduced and the background increases. From the viewpoint of the image density and backthe particle surface is not coated with these materials, due to poorer dispersibility of the magnetite particles in a vehicle The magnetic particle powder according to the invention is coated with Si oxide, Al oxide or a mixture thereof. If 22.5 % by weight, or more preferably from 19.5 % to 22 % by weight.

55

05

St

0ε

ground, the coating amount is preferably from 0.1 to 2.0 % by weight of the magnetite particle in terms of  $Al_2O_3$  and/ or  $SiO_2$ .

The specific surface area of the magnetic particle powder according to the invention is from 3.5 to 9.5 m<sup>2</sup>/g, preferably, 4.0 to 8.5 m<sup>2</sup>/g. If it is less than 3.5 m<sup>2</sup>/g, the dispersibility of the magnetite particles in the vehicle resin decreases and the background increases. If it is greater than 9.5 m<sup>2</sup>/g, the electrostatic properties of the toner decline and the image density decreases.

The magnetic particle powder according to this invention are typically in the form of a polyhedron, preferably a hexahedron or octahedron, or a sphere.

The magnetic particle powder according to this invention may be prepared by heat oxidation in an oxidizing atmosphere, at 350°C to 700°C, of magnetite particles synthesized from an aqueous solution containing Fe²+ and coated with the AI compound, Si compound or both of these compounds, or alternatively, by preliminary heat oxidation at 200 to 350°C followed by the heat oxidation at 350 to 700°C to convert them into maghemite/hematite composite particles coated with the aforesaid oxides, and then by thermal reduction in a reducing atmosphere at 250 to 500°C of the resultant composite particles.

In the preparation described in the foregoing, the magnetite particles obtained by the wet process are in the form of hexahedron, octahedron, polyhedron or sphere, and have the specific surface area of from 4 to 10 m²/g. In the wet process, an oxidizing gas may be passed at a temperature of from 60°C to 100°C into an aqueous solution of Fecontaining precipitate such as Fe(OH)<sub>2</sub> or FeCO<sub>3</sub>, obtained by mixing an aqueous solution of a ferrous salt such as ferrous sulfate with an aqueous solution of alkali such as sodium hydroxide or sodium carbonate, so as to give a black precipitate. Acid radicals are then washed out with water, and the product dried to prevent discoloration. In another method, an aqueous solution containing Fe<sup>2+</sup> and Fe<sup>3+</sup> in the ratio 1:2 is prepared using an aqueous solution of ferrous salt such as ferrous sulfate and an aqueous solution of ferric salt such as ferric sulfate, at least one equivalent of an aqueous solution of alkali such as NaOH is added, and the resulting mixture is heated to between 50° and 100°C to give a black precipitate. Acid radicals are then washed out with water, and the product dried to prevent discoloration.

In the above preparation method, the magnetite particles are coated with an Al compound, Si compound or both of these compounds. The Al compound may include aluminum sulfate, aluminum chloride, aluminum nitrate or sodium aluminate. The Si compound may include water glass, potassium silicate, sodium silicate or colloidal silica.

The magnetite particles may be soaked with an aqueous solution of the Al compound, Si compound, or both of Al and Si compounds. Alternatively, the magnetite particles may first be soaked with an aqueous solution of the Al compound, Si compound or both of Al and Si compounds, and an aqueous solution of acid or alkali added to cause deposition of Al oxide hydroxide or hydroxide, or of Si oxide hydroxide, on the surface of the magnetite particles. The latter method is to be preferred.

The heat oxidation temperature in this method is 350°C to 700°C. If the temperature is less than 350°C, the generation of hematite in the maghemite/hematite composite is insufficient, and only the magnetite particles having a low coercive force and residual magnetization are obtained. If the temperature is higher than 700°C, the magnetite particles having the residual magnetization in the specified range are obtained, but inter-particle sintering occurs so that the dispersibility in the vehicle resin is poorer.

In the preparation method described in the foregoing, a heat oxidation at 200°C to 350°C may, if necessary, be carried out prior to the heat oxidation at 350°C to 700°C. In this instance, it is possible to cause the magnetite particles to emit a considerable amount of heat in advance, and therefore it is easy to adjust the temperature when the starting particulate magnetite is converted to the particulate maghemite/hematite composite, to control the amount of hematite in the maghemite/hematite particles, and to control the residual magnetization of the magnetite particles.

If the temperature is less than 200°C, a considerable time is required to initiate the exothermic reaction of the magnetite particles. The sufficient heat may be emitted by the magnetite below 350°C, so there is no advantage in using higher temperatures.

The heat reduction temperature in the present invention is 250°C to 500°C. If it is less than 250°C, the reduction proceeds too slowly, and a considerable time is required to generate the magnetite particles. If it is higher than 500°C, the reduction proceeds too rapidly causing particle deformations and inter-particle sintering.

The preparation method, by which the amount of hematite in the particulate maghemite/hematite composite may be controlled, makes it possible to obtain the magnetite particles having the residual magnetization corresponding to the amount of hematite, and it is therefore easy to control the residual magnetization of the magnetite particles.

The above relation is represented in Fig. 1, of which data were derived from some experiments among many investigations conducted by the inventors. Fig. 1 shows the relation between the residual magnetization of the magnetite particles finally obtained and the amount of hematite in the maghemite/hematite composite particles. The latter composite particles were produced by the heat oxidation at 400 to 650 °C of three sorts of magnetite particles obtained from the aqueous solution, and the former magnetite particles as a final product were produced by the reduction of the latter composite particles thus obtained. The amount of hematite in the maghemite/hematite composite was expressed using measured values of the saturation magnetization of the composite. The smaller is the saturation magnetization,

5

10

15

20

25

35

40

45

# Eb 0 299 0 d3

the greater is the amount of non-magnetic hematite.

diameter:0.28 µm), respectively. as calculated in terms of Al<sub>2</sub>O<sub>3</sub> and with 0.54% by weight of Si oxide as calculated in terms of SiO<sub>2</sub> (mean average average diameter:0.35 µm), and another octahedral magnetite particle powder coated with 0.34% by weight of AI oxide octahedral magnetite particle powder coated with 0.25% by weight of Si oxide as calculated in terms of SiO<sub>2</sub> (mean by weight of Al oxide as calculated in terms of  $Al_2O_3$  (mean average diameter:0.30  $\mu$ m,  $SiO_2$  content:0.23% by weight), In Fig. 1, the lines X to Z correspond to SiO<sub>2</sub> containing spherical magnetite particle powder coated with 0.40%

particle surface is coated with Si oxide, Al oxide or a mixture thereof. magnetization, amount of Fe2+ and specific surface area are controlled to lie within the specific ranges, and that the consider that the advantages of the magnetic toner according to this invention are due to the facts that the residual surface of each particle, a magnetic toner having the desired properties cannot be obtained. The inventors therefore or a mixture thereof, or contain Si oxide, Al oxide or a mixture thereof only in the interior of the particles but not on the the specified range, have the specific surface area outside the specified range, are not coated with Si oxide, Al oxide the magnetite particles have the residual magnetization outside the specified range, contain an amount of Fe<sup>2+</sup> outside particle powder for the magnetic toners used in MICR. As shown by comparative examples hereinafter described, if can be read accurately. The magnetite particles of the invention can threfore be advantageously used as the magnetic by including them into the latter. If the toner thus obtained is used to form images, the images are finely accurate and The magnetite particles thus produced in accordance with the invention is used to manufacture a magnetic toner

**EXAMPLES** oz

ative examples, which are by no means limitative to the claimed invention hereinafter defined. This invention will now be illustrated in further detail with reference to specific preparation examples and compar-

mentioned in the foregoing, and in the following preparation examples and comparative examples were observed by The shapes of the particles obtained in the experiments conducted during the investigation of the invention, as

10 KO6. VSM-3S-15" manufactured by Toei Kogyo K.K.in Japan under the condition of applying an external magnetic field up The magnetic properties of the particle powder were measured by means of "Vibration Sample Magnetometer an electron microscope.

is to 100%, the higher is the reliability of reading Formation of Magnetite Particles from Aqueous Solution: as a proportion and percentage. The closer the signal level is to the nominal signal level, i.e., the closer the percentage of an image measured by an MICR Test Reader and the nominal signal level for the same image, and was expressed the relative signal levels as described in JIS X9002. The relative signal level was found by comparing the signal level a Macbeth Reflection Densimeter, and the reliability of reading the image was evaluated in relative terms by comparing Image quality was evaluated in relative terms by measuring the image density and the degree of background using

Table 1 shows the properties of magnetite particle powders A to F produced by the wet process involving an

oxidation reaction using an aqueous solution which contains  $\mathsf{Fe}^{2+}$ .

55

05

00

0ε

52

EP 0 566 790 B1

able 1

No.			Type of Magnetite Particle	etite Par	ticle	
	Shape	Average	Specific	Content	Residual	Content of
		Diameter	Surface area	of Fe2+	Magnetization	SiO <sub>2</sub>
		(IIII)	(m <sup>2</sup> /q)	(wt8)	(emu/q)	(wt 8)
ď	Particulate	0.31	3.5	18.2	8.5	1
B	Particulate	0.28	5.6	18.0	9.8	1
ວ	Particulate	0.22	7.3	17.9	10.4	-
D	Particulate	0.22	7.3	18.3	10.5	0.24
3	Particulate	0.15	6.8	15.1	13.2	0.05

Heat Treatment of Magnetite Particles Formed in the Foregoing:

Preparation Example 1

Sodium hydroxide was added to a suspension obtained by mixing 1 kg of magnetite perticle powder A with 10 l of

water to adjust the pH to 11. 17.2 g of # 3 water glass (supplied by Tokuyama Soda, Co., Ltd., containing 29 percent by weight as calculated in terms of  $\mathrm{SiO_2}$ ), corresponding to 0.5 percent by weight as calculated in terms of  $\mathrm{SiO_2}$ ), corresponding to 0.5 percent by weight as calculated in terms of  $\mathrm{SiO_2}$ , corresponding to 0.5 percent by stirring the mixture and sulfuric with respect to the starting magnetite particles, was then added thereto followed by stirring the mixture and sulfuric scid was added to adjust the pH to 9. This gave a black precipitate of the magnetite particles having an  $\mathrm{SiO_2}$  film deposited on their surfaces. The suspension containing this black precipitate was filtered, washed and dried.

Fluorescent X-ray spectroscopy showed that the amount of SiO<sub>2</sub> on the surface of the black particles obtained was 0.25 percent by weight as calculated in terms of SiO<sub>2</sub>.

One percent, magnetite particles coated with  $Sig^2$  was Introduced into a 3 I retort having one open end. Air was passed through at a rate of 5 I/min while rotating the retort, and at the same time the particles were heated at 300°C for 60 min, and were then heat oxidized at 390°C for 90 min to obtain a powder of a maghemite/hematite

A part of the above maghemite/hematite composite particle powder was taken out and subjected to a measurement of saturation magnetization, which was found to be 63.2 emu/g.

Thereafter, the atmosphere in the retort was replaced by  $M_2$ , and the flow gas was changed to 2 I of  $H_2$  gas/min while the contents of the retort were heat reduced at 340°C for 150 min to obtain a magnetite particle powder. Electron microscope observation showed that the particles of this resultant magnetite particle powder had the same shape as those of the starting magnetite particle and that they were distinctly separate from one another. The powder had a residual magnetisation  $\sigma_r$  of 13.5 emu/g, and contained 27.2 percent by weight of Fe²+. Its BET specific surface

area was 4.1 m²/g.
Preparation Example 2

Sodium hydroxide was added to a suspension obtained by mixing 1 kg of magnetite particle powder C with 10 l of water to adjust the pH to 9. 17.2 g of # 3 water glass (supplied by Tokuyama Soda, co., Ltd., containing 29 percent by weight of Si as calculated in terms of  $SiO_2$ ), corresponding to 0.5 percent by weight of  $SiO_2$  with respect to the starting magnetite powder, and 10.0 g of aluminum sulfate (supplied by Yoneyama Yakuhin Kogyo K.K., containing 30 percent by weight of Al $_2O_3$  with respect to the starting magnetite powder, were then added thereto and stirred, and sulfuric acid was then added thereto to adjust the starting magnetite powder, were then added thereto and stirred, and sulfuric acid was then added thereto to adjust the starting magnetite powder, were then added thereto and stirred, and sulfuric acid was then added thereto to adjust the starting magnetite powder, were then added the magnetite particles having aluminum hydroxide and  $SiO_2$  deposited pH to 7. This resulted in a black precipitate of the magnetite particles having aluminum hydroxide and  $SiO_2$  deposited

on their surfaces. The suspension containing this black precipitate was filtered, washed and dried. Fluorescent X-ray spectroscopy showed that the amounts of Si and AI on the surface of the blacks particles obtained were respectively 0.50 percent by weight as  $SiO_2$  and 0.20 percent by weight as  $AI_2O_3$ . One kg of these magnetite particles coated with  $SiO_2$  and  $AI_2O_3$  was introduced into a 3 I retort having one open end. Air was passed through every minute at a rate of  $SI_2O_3$  was introduced into a 3 I retort having one open end. Air was passed through every minute at a rate of  $SI_2O_3$  was introduced into a 3 I retort having one open end. Air was passed through every minute at a rate of  $SI_2O_3$  was introduced into a 3 I retort having one open end. Air was passed through

60 min and then heat oxidized at 530°C for 90 min to obtain a powder of maghemite/hematite composite.

A part of the above maghemite/hematite composite powder was taken out and subjected to a measurement of

saturation magnetization, which was found to be 21.5 emu/g. Thereafter, the atmosphere in the retort was replaced by  $M_2$ , and then the flow gas was changed to  $H_2$  at a rate of 5 l/min while the contents of the retort were heat reduced at 310°C for 220 min to obtain a magnetite particle powder. Electron microscope observation showed that the particles of this resultant magnetite powder had an average diameter of 0.27  $\mu$ m, the same shape as those of the starting magnetite particle, and they were distinctly separate from one another. The powder had a residual magnetisation  $\sigma_{\rm t}$  of 14.5 emu/g and contained 19.8 percent by weight of Fe<sup>2+</sup>. Its BET specific surface area was 8.4 m²/g.

Preparation Example 3

One kg of the magnetite particle powder C coated with AI oxide and Si oxide, which were produced in the same manner as described in Preparation Example 2, was introduced into a 31 retort having one open end. Air was passed through every minute at a rate of 51/min while rotating the retort, and at the same time the particles were heated at 300°C for 60 min and then heat oxidized at 560°C for 90 min to obtain a powder of a maghemite/hematite composite. A part of the above maghemite/hematite composite powder was taken out and subjected to a measurement of

saturation magnetization, which was found to be 10.8 emu/g. Thereafter, the atmosphere in the retort was replaced by  $M_2$ , and then the flow gas was changed to  $H_2$  at a rate of 5 l/min, while the contents of the retort were heat reduced at 320°C for 190 min to obtain a magnetite particle powder. Electron microscope observation showed that the particles of this resultant magnetite powder had an average diameter of 0.28  $\mu$ m, the same shape as those of the starting magnetite particle, and they were distinctly separate diameter of 0.28  $\mu$ m, the same shape as those of the starting magnetite particle, and they were distinctly separate of 0.28  $\mu$ m, the same shape as those of the starting magnetite particle, and they were distinctly separate of 0.28  $\mu$ m, the same shape as those of 18.3  $\mu$ m.

05

0t

SE

52

SO

SI

Preparation Examples 4 - 5 and Comparative Examples 1 - 2

Magnetite particle powders were obtained in the same manner as in Preparation Example 1, excepting that the type of starting magnetite powder, type and amount of coating material, heat oxidation temperature, oxidation time, reducing temperature and reducing time were varied in producing the magnetite particles. Table 2 shows the main producing conditions and properties of the products obtained.

99

05

SÞ

	Comparative Ex. 2	Comparative Ex. 1			Preparation 8x. 5		Preparation Bx. 4		Préparation Bx. 3		Preparation Bx. 2	Preparation Ex. 1		<b>Example</b> 3	Comparative	and	Preparation Examples S
	ъ	ט	,		₩		В		င		C	×			Particle		Starting
Aluminum Sulfate	#3 Water Glass	1	٠	Aluminum Sulfate	<b>∤3 Water Glass</b>	Aluminum Sulfate	#3 Water Glass	Aluminum Sulfate	#3 Water Glass	Aluminum Sulfate	#3 Water Glass	#3 Water Glass		Material	Coating		Coating Operation
0.3	0.5	}		0.5	0.5	0.5	0.5	0.3	0.5	0.3	0.5	0.5		(wt 8)	Amount		lon
290		300	380	290		290		300		300		300	Tempreture (°C)	Oxidation	Pre-heating		Preparation of Paticu
60		60	3	60		60		60		60		60	(min)	Time	Ing	Contr	of Paticu
600		·	570	570		520		560		.530		390	Tempreture (°C)	Omidation	Heat Oxidation	Composite	late Maghemite/Hematite
90		90	3	90	-	90		90		90		90	(n.j.n.)	Time	ation		[ematite

0\$ sε 0ε

52

50

SL

01

s

rable 2-

Preparation	Particulate	Prepara	Preparation of		•			
Bramples	Maghemite/Wematite Paticulate Magnetite	Paticulate	Magnetite		Paticula	te Magnet	Paticulate Magnetite powder	L
pue	Composite	aod	powder					
Comparative	Saturation	Reduction	Reduction Reduction	Average	Specific	Content	Residual	Coated Amo-
Saaroles	Magnetization	j.	Time	Diameter	Surface	of Fe <sup>2+</sup>	Magneti-	unt of \$1 or
	(6/ma)	(3.)	(mfm)	<u> </u>	Area	(wt.1)	ration	Al Onide
					(m <sup>2</sup> /q)		(ems/d)	(wt))
Preparation Bx. 1	63.2	340	150	0.39	4.1	21.2	13.5	0.25
Preparation Bx. 2	21.5	310	220	0.27	æ.	19.9	14.5	0.50
Preparation Ex. 3	10.8	320	190	0.20	8.1	20.7	16.3	0.50
Preparation Bx. 4	6.5	360	150	0.34	6.4	22.1	18.0 ,	0.51
Preparation Ex. 5	2.2	340	140	0.36	6.1	22.2	19.7	0.51
Comparātive Bx. 1	10.2	340	150	0.31	7.5	21.0	15.5	1
Comparative Ex. 2	1.7	320	180	0.36	6.0	20.4	20.5	0.51

Manufacture of Magnetic Toner:

# 55 Example 6

70 parts by weight of the magnetite particle powder obtained in Preparation Example 4, 100 parts by weight of styrene acrylic resin, 0.5 parts by weight of a negative charge control agent and 3 parts by weight of low molecular

# EB 0 299 0 d3

weight polypropylene were mixed together in a mixer at 140°C for 15 minutes, cooled, coarsely crushed and then finely ground. This finely ground substance was then classified pneumatically to give a magnetic toner, to which colloidal silica was added so as to obtain a negatively chargeable magnetic developer.

This developer was introduced into a Hewlett Packard Laser Jet Printer III, and used to form an image. The image was black with high density and very low background, and the fixedness was excellent. MICR output was also satistaction, and reliability of reading images was adequate.

Examples 7 - 15

Negatively changeable magnetic developers were prepared in the same manner as in Example 6 excepting that type of magnetic powder was varied. Images were formed using these negatively changeable magnetic developer in the same way as in Example 6. Table 3 shows the image properties and MICR characteristics.

The magnetite particle powder used in Example 13 was Mapico Black supplied by Cities Services, Co., and the accioular magnetite particle powder F used in Example 15 was a product of MTA-740 supplied by Toda Corp. (long axis: acioular magnetite particle powder F used in Example 15 was a product of MTA-740 supplied by Toda Corp. (long axis: 0.4 µm, aspect ratio (long axis:short axis) = 6.7, specific surface area: 19.9 m²/g, amount of Fe²+: 14.0 percent by weight as SiO₂).

so

01

52

0\$

05

32

0ε

	Image quality	wality		MICR Caractaristics	ristics	
Fixed-	Color	Image	Back-	Output	Re 11-	
by welght! ness		density	dround		ability	
S	Black	5	S	3	3	
5	Black	5	5	5	S	
						Evaluation: Each
5	Black	S	5	5	5	number is scored
						in line with the
•	Black	*	5	8	8	following criteria:
						1. Fairly bad
4	Black	3	•	-	4	2 Bad
						3. Acceptable
4	Black	4	2	-	2	4. Good
				2		5. Fairly good
	s s + + +		Black Black Black Black Black	Black 5 Black 5 Black 5 Black 4 Black 4	Black 5 5  Black 5 5  Black 4 5  Black 4 2	Black         5         5         5           Black         4         5         5           Black         4         5         5           Black         4         5         5           Black         4         2         4           Black         4         2         4           Black         4         2         4           Black         4         2         4           Black         4         2         4

Table 3-1

55

5

10

15

20

25

·6; 30

35

40

45

50

Example 2

55

o:	s
S	Þ
o	Þ
S	ε
o	ε
s	7
o	z

91	

01

S

Example	Haqnet i	Magnetite Particle		Image quality	vality		MICH Caracteristics	eristics	Evaluation: Each
	Type	Content of							number is scored
		Magnetite	Pixed-	Color	Image	Back-	Output	Reli-	line with the
		(Parts by weight) ness	ness		Density	ground		ability	following criteri
27 x . ds	Particulate			Reddish			2		1. Feirly bed
	Magnetite &	125	w	black	w	5	(Insufficient)	2	2. Bad
Bx. 9	Particulate			Slightly			2		3. Acceptable
	Magnetite B	155	w	Reddish black	w	5	(Insufficient)	2	4. Good
Ex. 16	Acicular			Reddish			1-4		5. Pairly good
	Magnetite F	45	w	Black	2	2	(Insufficient)		

following criteria:

number is scored i

#### Claims

5

10

15

20

25

30

35

- A magnetic particle powder which comprises magnetite particles coated with silicon oxide, aluminium oxide or a
  mixture thereof, has a residual magnetisation of from 12 to 20 Am<sup>2</sup>/kg (12 to 20 emu/g), contains from 18.5 to 22.5
  % by weight of Fe<sup>2+</sup> based on the total weight of the powder and has a specific surface area of from 3.5 to 9.5 m<sup>2</sup>/g.
- 2. A powder according to claim 1, wherein the residual magnetization is from 12 to 18.5 Am<sup>2</sup>/kg (12 to 18.5 emu/g).
- 3. A powder according to claim 1 or 2, wherein the content of Fe<sup>2+</sup> is from 19.5 to 22.5 % by weight.
- 4. A powder according to claim 3, wherein the content of Fe<sup>2+</sup> is from 19.5 to 22 % by weight.
- 5. A powder according to any one of the preceding claims, wherein the coating amount of Si and/or Al oxide is from 0.1 to 2.0 % by weight based on the total weight of the powder.
- 6. A powder according to any one of the preceding claims, wherein the specific surface area is from 4.0 to 8.5 m<sup>2</sup>/g.
- 7. A powder according to any one of the preceding claims, wherein each particle is in the form of a polyhedron or sphere.
- 8. A powder according to any one of the preceding claims, wherein the polyhedron is a hexahedron or octahedron.
- 9. A magnetic toner for use in magnetic image character recognition incorporating a magnetic particle powder as defined in any one of the preceding claims.

### Patentansprüche

- Pulver aus magnetischen Teilchen, welches Magnetitteilchen enthält, die mit Siliciumoxid, Aluminiumoxid oder einem Gemisch davon beschichtet sind, wobei das Pulver eine Restmagnetisierung von 12 bis 20 Am<sup>2</sup>/kg (12 bis 20 emu/g) besitzt, 18,5 bis 22,5 Gew.-% Fe<sup>2+</sup>, bezogen auf das Gesamtgewicht des Pulvers, enthält und eine spezifische Oberfläche von 3,5 bis 9,5 m<sup>2</sup>/g aufweist.
  - 2. Pulver gemäß Anspruch 1, wobei die Restmagnetisierung 12 bis 18,5 Am²/kg (12 bis 18,5 emu/g) beträgt.
- 3. Pulver gemäß Anspruch 1 oder 2, wobei der Gehalt an Fe<sup>2+</sup> 19,5 bis 22,5 Gew.-% beträgt.
- 4. Pulver gemäß Anspruch 3, wobei der Gehalt an Fe<sup>2+</sup> 19,5 bis 22 Gew.-% beträgt.
- 40 5. Pulver gemäß einem der vorstehenden Ansprüche, wobei die Menge an Silicium- und/oder Aluminiumoxid in der Beschichtung 0,1 bis 2,0 Gew.-%, bezogen auf das Gesamtgewicht des Pulvers, beträgt.
  - 6. Pulver gemäß einem der vorstehenden Ansprüche, wobei die spezifische Oberfläche 4,0 bis 8,5 m²/g beträgt.
- Pulver gemäß einem der vorstehenden Ansprüche, wobei jedes Teilchen die Form eines Polyeders oder einer Kugel aufweist.
  - 8. Pulver gemäß einem der vorstehenden Ansprüche, wobei das Polyeder ein Hexaeder oder ein Octaeder ist.
- Magnetischer Toner zur Verwendung bei der Erkennung von magnetischen Bildzeichen, wobei der Toner Pulver aus magnetischen Teilchen, wie in einem der vorstehenden Ansprüche definiert, enthält.

# R vendications

1. Poudre de particules magnétiques, qui comprend des particules de magnétite revêtues d'oxyde de silicium, d'oxyde d'aluminium ou d'un de leurs mélanges, possède une magnétisation ou aimantation résiduelle de 12 à 20 Am²/kg (12 à 20 emu/g), contient de 18,5 à 22,5 % en poids de Fe²+, sur la base du poids total de la poudre, et a une

surface spécifique de 3,5 à 9,5  $m^2/g$ .

- 2. Poudre selon la revendication 1, dans le cas de laquelle l'aimantation résiduelle est de 12 à 18,5 Am²/kg (12 à 18,5 emu/g).
- 3. Poudre selon la revendication 1 ou 2, dans le cas de laquelle la teneur en Fe<sup>2+</sup> est de 19,5 à 22,5 % en poids.
- 4. Poudre selon la revendication 3, dans laquelle la teneur en Fe<sup>2+</sup> est de 19,5 à 22 % en poids.
- 5. Poudre selon l'une quelconque des revendications précédentes, dans laquelle la proportion de revêtement par de l'oxyde de Si et/ou par de l'oxyde de Al est de 0, 1 à 2,0 % en poids, sur la base du poids total de la poudre.
- 6. Poudre selon l'une quelconque des revendications précédentes, dans le cas de laquelle la surface spécifique est de 4,0 à 8,5 m²/g.
- 7. Poudre selon l'une quelconque des revendications précédentes, dans laquelle chaque particule a la forme d'un polyèdre ou d'une sphère.
- 8. Poudre selon l'une quelconque des revendications précédentes, dans laquelle le polyèdre est un hexaèdre ou un 20 octaèdre.
- "Toner" (encre solide) magnétique destiné à servir dans une reconnaissance de caractères d'image magnétique, cette encre solide ou toner incorporant une poudre de particules magnétiques selon la définition indiquée dans l'une quelconque des revendications précédentes.

SZ

SI

s

0Е

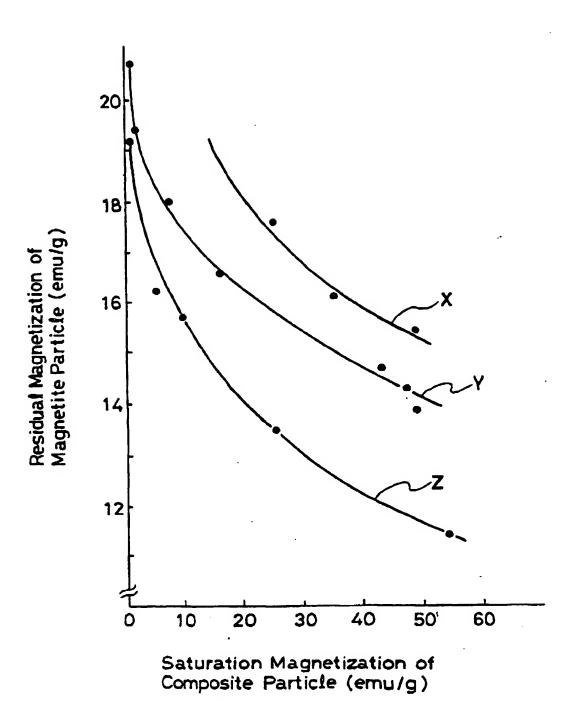
32

0*†* 

05

St

Fig. 1



· · ·